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SOVIET WORK ON CHROMATHERMOGRAPHIC SEPARATION

[The following report presents an account of work by a group of USSR investigators on the chromathermographic method of separation. The data was taken from sources listed at the end of this report.]

The classical chromatographic method of separation cannot be applied to mixtures which contain both easily adsorbable components and components that are adsorbed with difficulty. For instance, mixtures which contain both heavy and light hydrocarbons cannot be separated in this manner. The elution (displacement) and thermal methods of chromatographic separation have been proposed for such mixtures. However, the selection of a suitable eluent often presents difficulties. The method of thermal desorption, generally speaking, cannot be expected to give satisfactory results: the components will simply move in front of the electric furnace or other heating appliance without separating as the heating appliance is advanced along the chromatographic column. While neither the elution method nor the thermal method is satisfactory as such, a method which combines the advantages of both, i.e., the chromathermographic method, is of considerable practical value.

Chromathermography is a new method which occupies an intermediate position between ordinary chromatography and fractional distillation. In chromathermography, the mixture to be separated is acted upon simultaneously by a solvent (eluent) and a moving temperature field. Solution of differential equations which express the dynamics of the process shows that in chromathermography, as distinguished from other types of chromatography, the layers are compressed, as the substance being adsorbed moves along, to the thickness of a mathematical line in the case of a straight line isotherm, and to a thickness corresponding to asymptotic distribution in the case of a curvilinear isotherm.

It also follows from the mathematical treatment that the individual layers will have rigidly defined positions. The compression of the layers results in a high separation efficiency of the method. An expression for the coefficient of enrichment has been derived which indicates the increase of concentration obtained as a result of subjecting substances to the chromathermographic procedure. It has been demonstrated that in the case of asymptotic distribution the maximum concentration corresponds to the equilibrium concentration. On the basis of this, a simple method has been proposed for determining the thermal equation of adsorption by measuring the concentration and temperatures at the maximum of the yield curve. With the aid of this method, the heats of adsorption of individual substances can be determined.

Chromathermography is not simply a combination of development chromatography and thermal desorption. Application of a temperature gradient at the time when development is carried out introduces qualitatively new factors. In all types of chromatography with the exception of chromathermography, broadening of the layer of the adsorbed substance takes place. In chromathermography, as already mentioned, compression of the layer occurs as the substance moves through the thickness of the adsorbent. The reason for the compression is that the trailing boundary of the layer moves more rapidly than the leading boundary. This difference in velocity is due to the fact that the trailing boundary has a higher temperature than the front boundary of the layer.

Theory and experimental results show that in chromathermography all substances move with the same velocity, which is equal to the velocity of the source of heat, at temperatures that have a characteristic value for every substance contained in the mixture being separated. The compression of layers and movement of compounds within definite temperature intervals make the method suitable not only for the quantitative but also for the qualitative analysis of mixtures. Application of a

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temperature field in chromathermography permits variation of the capacity of the adsorbent within a wide range, so that the separation of complex mixtures which contain both easily adsorbable components and components that are adsorbed with difficulty is possible on the same adsorbent.

The fact that the layers of adsorbates can be narrowed in chromathermography is of great importance not only for analytical applications, but also because it enables one to increase concentrations of valuable substances which are present in very small quantities. For instance, natural gas contains a number of isocompounds that are extremely valuable to the petroleum conversion industry. However, these isocompounds are present only in very small quantities, so that they rarely can be detected and isolated by ordinary methods. Chromathermography permits their detection and isolation.

In work of this type done by the Institute of Geophysical and Geochemical Methods of Prospecting, Moscow, determination of hydrocarbons after they had passed through the layer of the adsorbent was carried out by means of a continuously operating thermochemical gas analyzer (a recording appliance the operation of which is based on the heat effect produced by combustion). This gas analyzer had a large operating volume. However, even when a gas analyzer of lower precision is used, the concentration of heavy hydrocarbons may be multiplied by a figure amounting to several hundred. With the use of appropriate recording devices, it will be possible to increase the coefficient of enrichment still further.

Chromathermographs for analytical purposes could not be introduced extensively into industrial practice because of the unavailability of cheap and simple gas analyzers suitable for continuous operation. The gas interferometer is too expensive, while a thermochemical analyzer or heat conductivity analyzer is too complicated and unreliable. For these reasons, the Institute of Geophysical and Geochemical Methods of Prospecting designed a chromathermograph which analyzes discontinuously 100 cc gas samples. In this model, the adsorption column is equipped with a stationary rather than a movable electric heater. Carbon dioxide is used as the solvent (eluent). The gases are measured volumetrically in a gas burette filled with potassium hydroxide solution, i.e., a solution which dissolves the carbon dioxide. Mixtures of methane, ethane, propane, and butane can be readily analyzed by means of this chromathermograph. Seven-component hydrocarbon mixtures (methane, ethane, ethylene, propane, propene, butane, and isobutene) could be analyzed accurately by means of an experimental chromathermograph equipped with an electrical heater moved along the column at a definite speed by a clockwork. Air was used as an eluent.

SOURCES

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